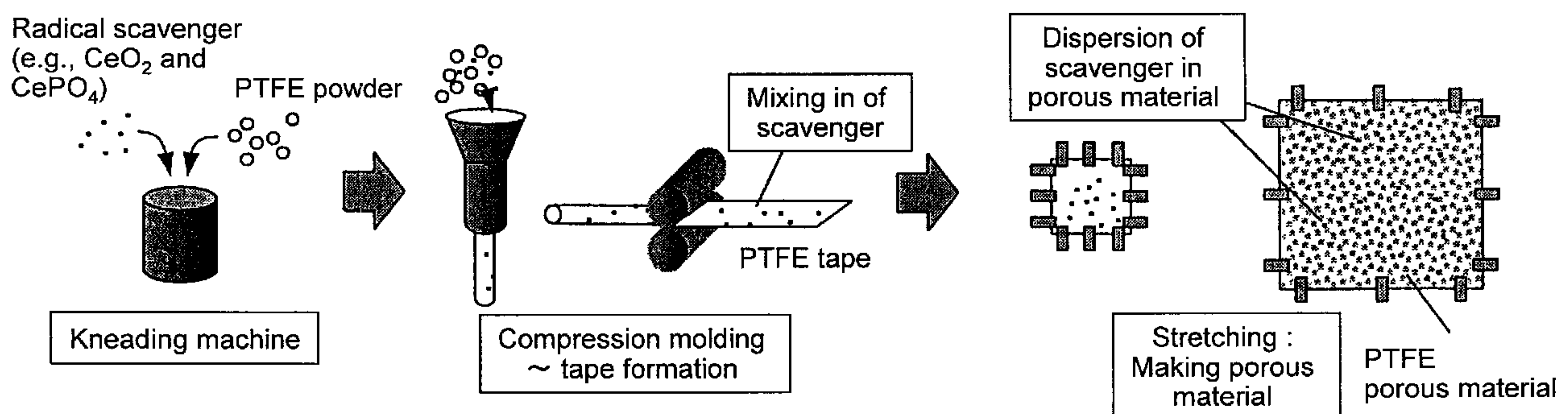




(86) Date de dépôt PCT/PCT Filing Date: 2007/08/23
(87) Date publication PCT/PCT Publication Date: 2008/03/06
(45) Date de délivrance/Issue Date: 2012/07/24
(85) Entrée phase nationale/National Entry: 2009/02/03
(86) N° demande PCT/PCT Application No.: JP 2007/066823
(87) N° publication PCT/PCT Publication No.: 2008/026666
(30) Priorité/Priority: 2006/08/28 (JP2006-230556)

(51) Cl.Int./Int.Cl. *H01M 8/02* (2006.01),
H01M 8/10 (2006.01)
(72) Inventeur/Inventor:
TAKESHITA, SHINYA, JP
(73) Propriétaire/Owner:
TOYOTA JIDOSHA KABUSHIKI KAISHA, JP
(74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : MEMBRANE D'ELECTROLYTE RENFORCEE POUR UNE PILE A COMBUSTIBLE, PROCEDE POUR SA FABRICATION, ENSEMBLE MEMBRANE-ELECTRODE POUR UNE PILE A COMBUSTIBLE ET PILE A COMBUSTIBLE DE TYPE POLYMERE SOLIDE AYANT L'ENSEMBLE
(54) Title: REINFORCED ELECTROLYTE MEMBRANE FOR FUEL CELL, METHOD FOR PRODUCING THE MEMBRANE, MEMBRANE-ELECTRODE ASSEMBLY FOR FUEL CELL, AND POLYMER ELECTROLYTE FUEL CELL COMPRISING THE ASSEMBLY



(57) **Abrégé/Abstract:**

A reinforced electrolyte membrane for a fuel cell wherein the electrolyte membrane is reinforced with a porous membrane and a radical scavenger is immobilized in the porous membrane. The reinforced electrolyte membrane for a fuel cell is a solid polymer electrolyte membrane suppressing the radical scavenger from leaking outside of the system and having good chemical durability.

* * * *

Abstract

A reinforced electrolyte membrane for a fuel cell wherein the electrolyte membrane is reinforced with a porous membrane and a radical scavenger is immobilized
5 in the porous membrane. The reinforced electrolyte membrane for a fuel cell is a solid polymer electrolyte membrane suppressing the radical scavenger from leaking outside of the system and having good chemical durability.

DESCRIPTION

REINFORCED ELECTROLYTE MEMBRANE FOR FUEL CELL, METHOD FOR
PRODUCING THE MEMBRANE, MEMBRANE-ELECTRODE ASSEMBLY FOR
5 FUEL CELL, AND POLYMER ELECTROLYTE FUEL CELL COMPRISING THE
ASSEMBLY

Technical Field

The present invention relates to a reinforced electrolyte membrane to be used for
10 fuel cells, a method for producing the membrane, a membrane-electrode assembly for
fuel cells, and a polymer electrolyte fuel cell comprising the assembly.

Background Art

Polymer electrolyte fuel cells have a structure comprising a solid polymer
15 electrolyte membrane as an electrolyte and electrodes bonded to both sides of this
membrane.

The polymer solid electrolyte membrane must have low membrane resistance
within itself when it is used in a fuel cell. Therefore, it is desired that such membrane
be as thin as possible. However, a solid polymer electrolyte membrane with too thin a
20 membrane has been problematic in that: pinholes occur during membrane production;
the membrane is torn or broken during electrode formation; and a short circuit easily
occurs between the electrodes. Moreover, a solid polymer electrolyte membrane used
in a fuel cell is always used in a wet state. Therefore, such a solid polymer electrolyte
membrane tends to have reliability problems, such as pressure resistance or cross-leaks
25 during differential pressure operation, resulting from swelling, deformation, and the like
of the polymer membrane caused by wetting.

Hence an electrolyte membrane for fuel cells that is reinforced with a porous
support has been developed.

Meanwhile, fluoride-based and hydrocarbon-based electrolyte membranes that

are used for polymer electrolyte fuel cells become thinner when electrolyte polymers deteriorate due to OH radicals generated upon generation of electric power. A means for suppression of such deterioration involves adding a radical scavenger represented by CeO_2 to a catalyst layer or a diffusion layer of MEA, so as to improve the resistance of
5 MEA to radicals.

In this case, the radical scavenger added to the catalyst layer or the diffusion layer migrates into the membranes with time. Aside from this, there is a method that involves adding a radical scavenger directly to electrolyte membranes. Furthermore, for the purpose of obtaining a membrane electrode assembly (MEA) for fuel cells
10 capable of suppressing OH radical attack against a proton ion conductive solid polymer membrane and retaining stable performance for a long time, JP Patent Publication (Kokai) No. 2005-190752 A discloses an invention relating to a membrane electrode assembly in which: a catalyst layer side of a gas diffusion electrode provided with a catalyst layer and a gas diffusion layer is arranged to be the solid polymer membrane
15 side on both faces of the proton-ion conductive solid polymer membrane; and a protective layer containing a component for improving oxidation resistance, such as a radical scavenger or a hydroperoxide decomposer, in a polymer material is interposed at the joined face between the solid polymer membrane and the catalyst layer.

However, such conventional art is problematic in that a radical scavenger is not
20 immobilized within the MEA, so that the effects of exertion of radical resistance are lowered when additives leak outside the MEA due to membrane swelling, flooding, or the like.

Specifically, a radical scavenger is not immobilized within an MEA. At the time of electric power generation, movement of water, such as membrane swelling, membrane contraction, or flooding due to generated water, constantly takes place within
25 the MEA due to electrophoresis of water or drying and wetting. When an additive is not immobilized, a radical scavenger migrates within the MEA via the movement of water, so as to leak out from the MEA.

Disclosure of the Invention

An object of the present invention is to provide a solid polymer electrolyte membrane that is capable of suppressing a radical scavenger from leaking outside of the system and has good chemical durability, and to provide a method for producing the same. Another object of the present invention is to provide a membrane-electrode assembly for fuel cells with improved chemical durability. Still another object of the present invention is to provide a polymer electrolyte fuel cell that has high electric power generation performance and good chemical durability by the use of such membrane-electrode assembly.

The present inventor has discovered that the above objects can be achieved by immobilizing a radical scavenger in a porous membrane of a reinforced electrolyte membrane, thereby achieving the present invention.

Specifically, a first aspect of the present invention is an invention of an electrolyte membrane for a fuel cell, which is reinforced with a porous membrane, in which a radical scavenger is immobilized in the porous membrane.

An example of the form of immobilization is, first, a form in which the radical scavenger is interposed within the porous membrane. Here, the expression, "a form in which the radical scavenger is interposed within the porous membrane," means that a radical scavenger adheres to a porous material forming the porous membrane. That is, examples of such form include a state in which a radical scavenger is implanted within the network structure of the porous membrane, a state in which a radical scavenger is embedded in the porous membrane, and a state in which a radical scavenger is sandwiched between meshes of the porous membrane.

Here, the term "immobilization" refers to, as described above, not only a case in which a radical scavenger remains on-site because of the porous material forming the porous membrane, but also a case in which a radical scavenger is adhered to the porous membrane with the use of an adhesive.

The hardness of a porous material forming the porous membrane is preferably of a lesser degree than that of the radical scavenger, since the radical scavenger is easily

interposed within the porous membrane.

Furthermore, the mean particle size of the radical scavenger is preferably larger than the mean pore size of the porous membrane in order to achieve immobilization of a radical scavenger in a porous membrane. This is because the radical scavenger is easily
5 caught in the meshes of the porous membrane, so that the leaking of the radical scavenger outside of the system can be suppressed.

As a radical scavenger to be used in the reinforced electrolyte membrane for a fuel cell of the present invention, in particular an inorganic or an organic compound having radical scavenging ability is widely used from among those added as
10 anti-oxidation agents in various materials. Among them, one or more of radical scavenger selected from the group consisting of CeO_2 , Ru, Ag, RuO_2 , WO_3 , FeO_4 , CePO_4 , CrPO_4 , AlPO_4 , FePO_4 , CeF_3 , FeF_3 , Fe-porphine, and Co-porphine are preferable examples.

When a radical scavenger to be used in the reinforced electrolyte membrane for
15 a fuel cell of the present invention is immobilized within a porous membrane, the particle size is preferably 100 μm or less and is more preferably 1 μm or less. Immobilization of a radical scavenger having a small particle size enables high dispersion of the radical scavenger in a PTFE porous membrane when a PTFE tape or the like is stretched.

20 When the particle size of a radical scavenger is 1 μm or less, the radical scavenger is caught in the pores of the porous membrane and thus immobilized or is embedded within the fibers of the porous membrane and thus immobilized. Figure 1 schematically shows a state in which a radical scavenger is embedded within the fibers of the porous membrane and a state in which a radical scavenger is caught in the pores of
25 the porous membrane and thus immobilized.

As porous membranes, those known as reinforced membranes for fuel cells can be used widely. For example, porous substrates made of fluorine-based resins having good strength and good shape stability, such as polytetrafluoroethylene, a polytetrafluoroethylene-chlorotrifluoroethylene copolymer, polychlorotrifluoroethylene,

polybromotrifluoroethylene, a polytetrafluoroethylene-bromotrifluoroethylene copolymer, a polytetrafluoroethylene-perfluorovinylether copolymer, or polytetrafluoroethylene-hexafluoropropylene copolymer, are preferably used. The degree of polymerization or the molecular weight of such a fluorine-based resin is not particularly limited. In view of strength, shape stability, and the like, the weight-average molecular weight of such a fluorine-based resin preferably ranges from approximately 10,000 to 10,000,000. Among these examples, a preferable example of a membrane substrate is polytetrafluoroethylene (PTFE), which can be easily made porous by drawing.

Specifically, a second aspect of the present invention is an invention of a method for producing an electrolyte membrane for a fuel cell that is reinforced with a porous membrane wherein a radical scavenger is immobilized in the porous membrane. The method for producing an electrolyte membrane for a fuel cell comprises at least the steps of kneading a porous material for the formation of the porous membrane with the radical scavenger and compression-molding the thus kneaded product. A state in which a radical scavenger is immobilized in the above porous membrane can be created by kneading a porous material for the formation of the porous membrane with the radical scavenger.

A specific example of such a production method is a method that comprises the steps of kneading the raw material powders or pellets for a porous membrane with a radical scavenger, compression-molding the thus kneaded product to form a tape, and then stretching the tape to make it porous. By the addition of a radical scavenger during the step of producing a porous membrane, the reinforced membrane can continuously have its own radical trapping function. Furthermore, according to the present invention, an electrolyte membrane for a fuel cell in which a radical scavenger is immobilized in a porous membrane can be produced without forming a tape or stretching a tape, depending on the selection of the porous material.

Specific examples of a radical scavenger, CeO_2 as a preferable example of such radical scavenger, specific examples of a raw material for a porous membrane, and

polytetrafluoroethylene (PTFE) as a preferable example of such raw material are as described above.

A third aspect of the present invention is an invention of a reinforced electrolyte membrane for a fuel cell, which is produced by the above method.

5 A fourth aspect of the present invention is an invention of a membrane-electrode assembly (MEA) for a fuel cell comprising the above reinforced electrolyte membrane for a fuel cell, which contains a pair of electrodes comprising a fuel electrode to which a fuel gas is supplied and an oxygen electrode to which an oxidizing agent gas is supplied and a polymer electrolyte membrane sandwiched between the pair of electrodes. The
10 electrolyte membrane for a fuel cell is characterized in that the polymer electrolyte membrane is reinforced with the above porous membrane and the radical scavenger is immobilized in the porous membrane.

A fifth aspect of the present invention is an invention of a polymer electrolyte fuel cell comprising a membrane-electrode assembly that has an electrolyte membrane
15 for a fuel cell, wherein the electrolyte membrane is reinforced with the above porous membrane and a radical scavenger is immobilized in the porous membrane.

The electrolyte membrane for a fuel cell according to the present invention is provided, in which the electrolyte membrane is reinforced with a porous membrane and a radical scavenger is immobilized in the porous membrane. Specifically, the radical
20 scavenger is present being adhered to or embedded within the porous material. Hence, when the membrane is used as a reinforcement layer for electrolytes, the radical scavenger merely leaks outside of the system, the effect of radical resistance is long lasting, and the membrane can be prevented from becoming thinner due to the leakage of the radical scavenger outside of the system. Furthermore, the method of the present
25 invention for producing an electrolyte membrane for fuel cells, according to which the electrolyte membrane is reinforced with a porous membrane and a radical scavenger is immobilized in the porous membrane, enables high dispersion of the radical scavenger in the porous material by stretching a PTFE tape or the like supplemented with a radical scavenger.

As a result, the electrolyte membrane for a fuel cell of the present invention has improved chemical durability and good mechanical strength, since it is reinforced with a porous membrane. Thus, the durability of the fuel cell can be improved. Furthermore, a polymer electrolyte fuel cell producing high output and having good durability can be
5 obtained by the use of the electrolyte membrane for a fuel cell, in which the electrolyte membrane is reinforced with a porous membrane and a radical scavenger is immobilized in the porous membrane.

Brief Description of the Drawings

10 Fig. 1 schematically shows a state in which radical scavengers are embedded within the fibers of a porous membrane and a state in which radical scavengers are caught and immobilized in pores of a porous membrane. Fig. 2 shows an outline of the method of the present invention for producing a reinforced electrolyte membrane for a fuel cell.

15

Best Mode for Carrying Out the Invention

The present invention is described as follows according to the outline of the method for producing a reinforced electrolyte membrane for a fuel cell shown in Fig. 2. Raw material powders or pellets of a porous membrane such as PTFE and a radical
20 scavenger such as CeO_2 or CePO_4 are added to a kneading machine, and then the mixture is kneaded. Next, the kneaded product that has been subjected to compression-molding is formed into a tape using a roller. At this time point, the radical scavenger is highly dispersed and mixed in the PTFE tape. Next, the tape is stretched to make it porous. The radical scavenger is immobilized in the porous membrane. As described above, an
25 electrolyte membrane for a fuel cell, in which the electrolyte membrane is reinforced with a porous membrane and a radical scavenger is immobilized in the porous membrane, is easily produced by the addition of the radical scavenger during the step of producing the porous membrane. Moreover, such reinforced membrane itself can continuously have a radical trapping function.

The polymer electrolyte fuel cell of the present invention is a polymer electrolyte fuel cell produced using the above electrolyte membrane of the present invention for a fuel cell, in which a radical scavenger is immobilized in the porous membrane, for a membrane-electrode assembly. The polymer electrolyte fuel cell can be produced to have the constitution of a generally known polymer electrolyte fuel cell, except for using the electrolyte membrane for a fuel cell of the present invention.

The present invention will now be described in more detail with reference to examples and comparative examples.

[Example 1]

PTFE powders were mixed with 5 wt% CePO_4 powders (mean particle size: 1 μm). After the steps of molding $\Rightarrow$ tape formation $\Rightarrow$ stretching, a PTFE porous material containing CePO_4 was produced. Nafion* solution DE2020 (trade name, DuPont) was casted on the PTFE porous material, so that an electrolyte membrane containing a reinforcement layer was produced (referred to as electrolyte A).

A catalyst layer was transferred to the electrolyte A, carbon paper was used as a diffusion layer, and then MEA was produced (referred to as MEA (A)).

[Example 2]

PTFE powders were mixed with 5 wt% CePO_4 powders (mean particle size: 0.1 μm). After the steps of molding $\Rightarrow$ tape formation $\Rightarrow$ stretching, a PTFE porous material containing CePO_4 was produced. Nafion* solution DE2020 (trade name, DuPont) was casted on the PTFE porous material, so that an electrolyte membrane containing a reinforcement layer was produced (referred to as electrolyte B).

A catalyst layer was transferred to the electrolyte A, carbon paper was used as a diffusion layer, and then MEA was produced (referred to as MEA (B)).

[Comparative example 1]

Aside from the electrolyte membrane A, CePO_4 powders (mean particle size: 1 μm) were dispersed in the same amount as that of the electrolyte membrane A in Nafion* solution DE2020 (trade name, DuPont). The dispersion was casted on an additive-free PTFE porous material, so that an electrolyte membrane was produced (referred to as

* Trade-mark

electrolyte C).

A catalyst layer was transferred to the above electrolyte B carbon paper was used as a diffusion layer, and then MEA was produced (referred to as MEA (C)).

[Comparative example 2]

- 5 CePO₄ powders were not added to Nafion* solution DE2020 (trade name, DuPont) and a PTFE porous material. CePO₄ was added to a cathode catalyst layer and then MEA was produced using the same (referred to as MEA (D)).

[Comparative example 3]

- 10 Nafion* solution DE2020 (trade name, DuPont) was casted on a PTFE porous material and then MEA was produced without adding any additive (referred to as MEA (E)).

[Performance assessment]

Output voltages at 0.1 A/cm² of the above MEA (A) to (E) were compared by a durability test. Table 1 below shows the results of comparing output voltages.

15

Table 1

		Output voltage (V)		
		Initial	After 1000 hours	After 3000 hours
Example 1	MEA (A)	0.80	0.79	0.76
Example 2	MEA (B)	0.81	0.79	0.75
Comparative example 1	MEA (C)	0.79	0.76	0.66
Comparative example 2	MEA (D)	0.80	0.78	0.70
Comparative example 3	MEA (E)	0.82	0.45	-

- 20 As can be noted in the results in Table 1, both MEA (A) and MEA (B) (produced in Examples using the electrolyte membrane for a fuel cell, in which the electrolyte membrane had been reinforced with the porous membrane and the radical scavenger had been immobilized in the porous membrane) were equivalent to MEA (C) (produced using the electrolyte membrane for a fuel cell of Comparative example 1, in which no radical

* Trade-mark

scavenger had been immobilized), MEA (D) (produced using the electrolyte membrane for a fuel cell of Comparative example 2, in which the radical scavenger had been added not to a porous membrane but to a cathode catalyst layer), and MEA (E) (produced without using the electrolyte membrane for a fuel cell of Comparative example 3, in which no radical scavenger had been immobilized) in terms of initial output voltage. Furthermore, both MEA (A) and MEA (B) maintained the initial output voltages longer than MEA (C), MEA (D), and MEA (E). According to the present invention, a radical scavenger adheres to or is embedded in a porous material, so that the radical scavenger merely leaks outside of the system, the effect of radical resistance is maintained, and the durability of the fuel cell is significantly improved.

Industrial Applicability

The electrolyte membrane for a fuel cell of the present invention is reinforced with a porous membrane and a radical scavenger is immobilized in the porous membrane. Hence, a polymer electrolyte fuel cell having high output and good durability can be obtained with the use of the electrolyte membrane for a fuel cell, thereby contributing to practical application and the spread of fuel cells.

What is claimed is:

1. A reinforced electrolyte membrane for a fuel cell, wherein the electrolyte membrane is reinforced with a porous membrane, and particles of a radical scavenger are interposed and immobilized in the porous membrane so as to suppress leakage of the radical scavenger particles from the reinforced electrolyte membrane,
wherein the radical scavenger is one or more selected from the group consisting of CeO_2 , Ru, Ag, RuO_2 , WO_3 , Fe_3O_4 , CePO_4 , CrPO_4 , AlPO_4 , FePO_4 , CeF_3 , FeF_3 , Fe-porphine, and Co-porphine.
2. The reinforced electrolyte membrane for a fuel cell according to claim 1, wherein hardness of a porous material for the formation of the porous membrane is of a lesser degree than that of the radical scavenger particles so that the radical scavenger particles are embedded in the porous material forming the porous membrane.
3. The reinforced electrolyte membrane for a fuel cell according to claim 1, wherein mean particle size of the radical scavenger particles is larger than the mean pore size of the porous membrane so that the radical scavenger particles are caught within the porous membrane.
4. The reinforced electrolyte membrane for a fuel cell according to any one of claims 1 to 3, wherein the porous membrane is a polytetrafluoroethylene (PTFE) membrane.
5. A method for producing a reinforced electrolyte membrane for a fuel cell wherein the electrolyte membrane is reinforced with a porous membrane and particles of a radical scavenger are interposed and immobilized in the porous membrane, the method comprising at least the steps of:
kneading raw material powder or pellets for the formation of the porous membrane with the radical scavenger particles;
compression-molding a kneaded product; and

providing an electrolyte material to a compression molded product to form the reinforced electrolyte membrane.

6. The method for producing a reinforced electrolyte membrane for a fuel cell according to claim 5, wherein the step of compression molding the kneaded product is the step of forming a tape by compression molding of the kneaded product and the method comprises the step of stretching the tape to make it porous.
7. The method for producing a reinforced electrolyte membrane for a fuel cell according to claim 5 or 6, wherein the radical scavenger is one or more selected from the group consisting of CeO_2 , Ru, Ag, RuO_2 , WO_3 , Fe_3O_4 , CePO_4 , CrPO_4 , AlPO_4 , FePO_4 , CeF_3 , FeF_3 , Fe-porphine, and Co-porphine.
8. The method for producing a reinforced electrolyte membrane for a fuel cell according to any one of claims 5 to 7, wherein a raw material of the porous membrane is polytetrafluoroethylene (PTFE).
9. A reinforced electrolyte membrane for a fuel cell, which is produced by the method according to any one of claims 5 to 8.
10. A membrane-electrode assembly for a fuel cell comprising a pair of electrodes composed of a fuel electrode to which a fuel gas is supplied and an oxygen electrode to which an oxidizing agent gas is supplied and a polymer electrolyte membrane sandwiched between the pair of electrodes, wherein the polymer electrolyte membrane is the reinforced electrolyte membrane for a fuel cell according to any one of claims 1 to 4.
11. A polymer electrolyte fuel cell comprising a membrane-electrode assembly having the reinforced electrolyte membrane for a fuel cell according to any one of claims 1 to 4.

Fig. 1

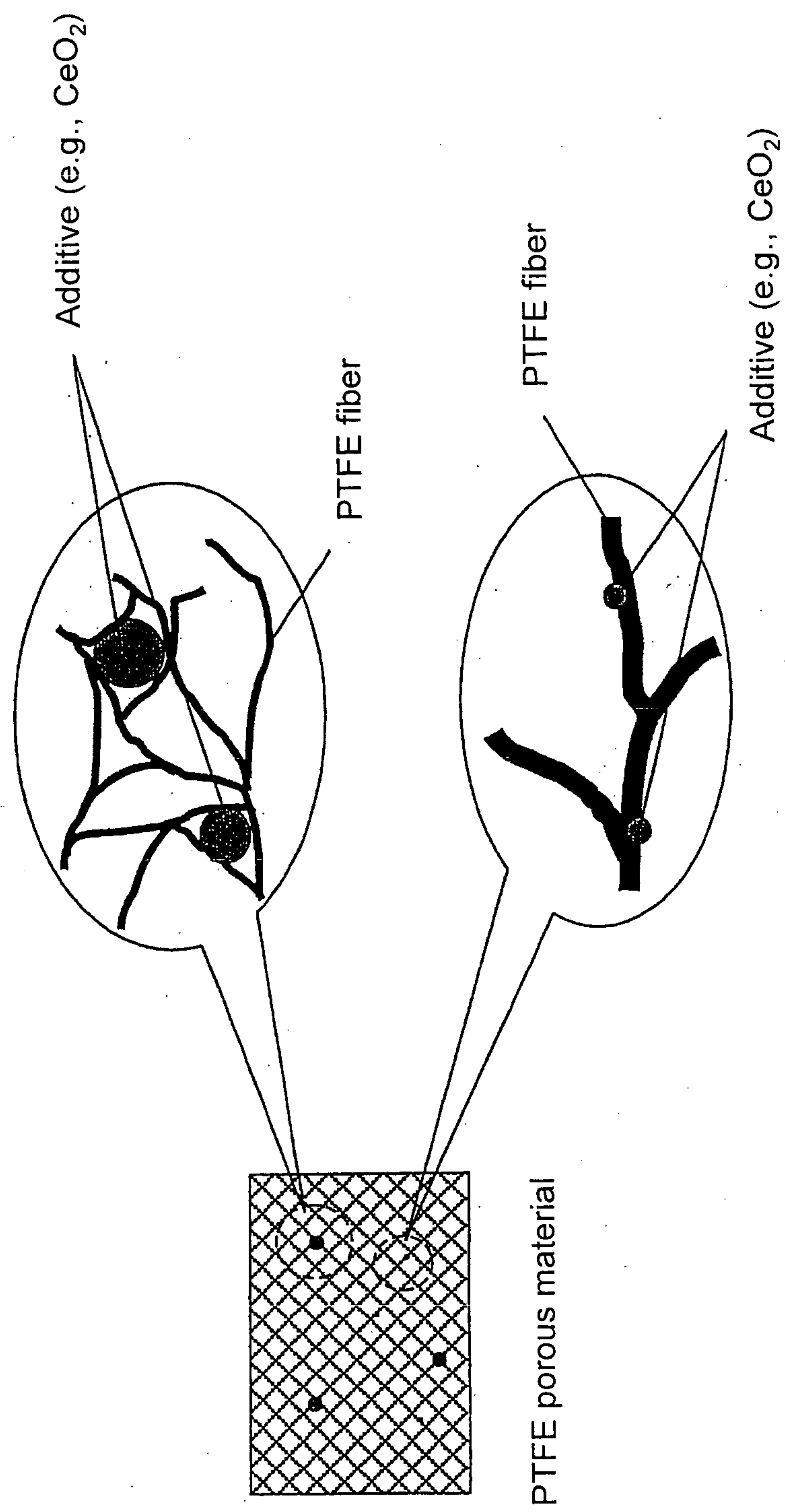


Fig. 2

